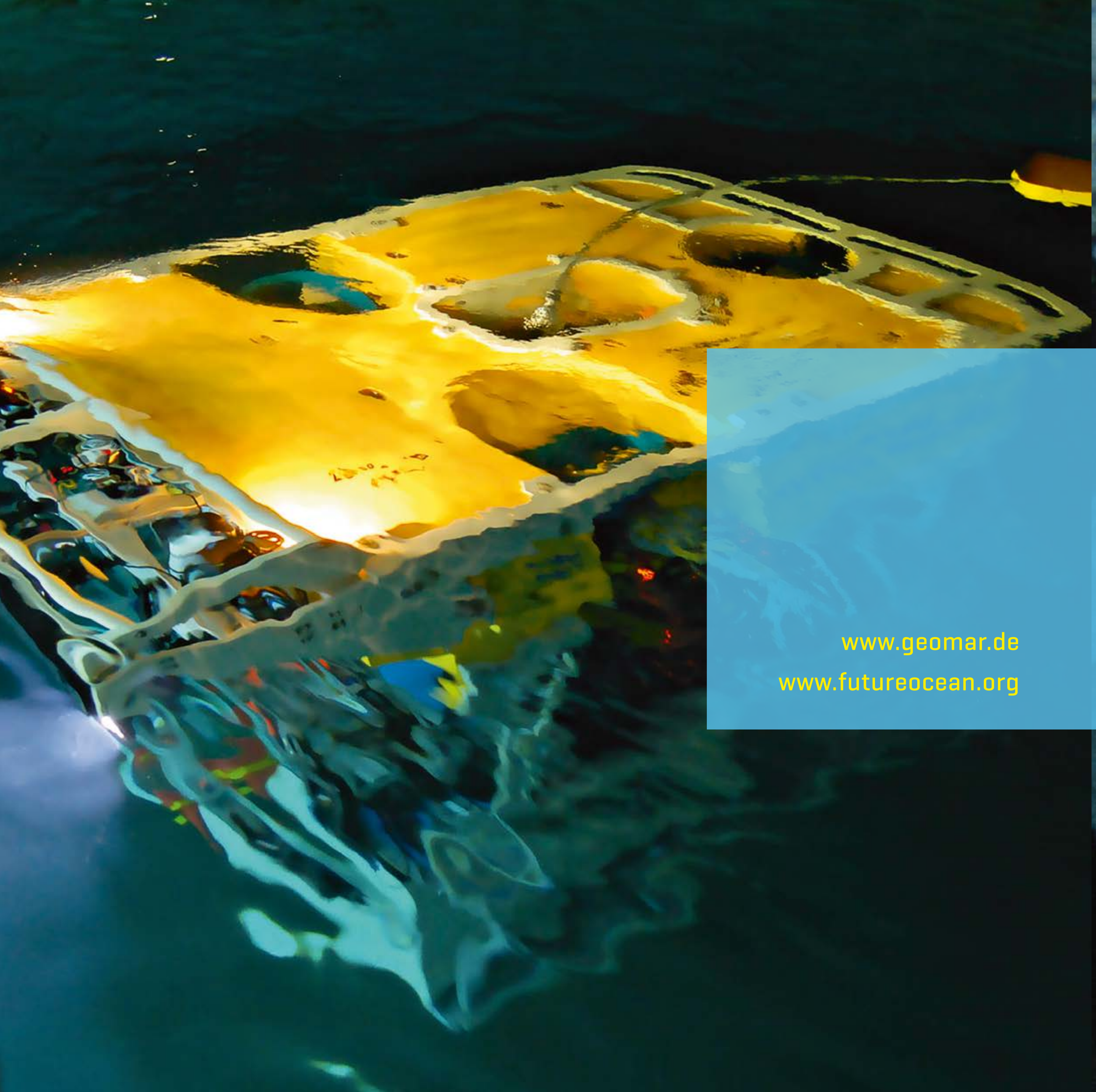

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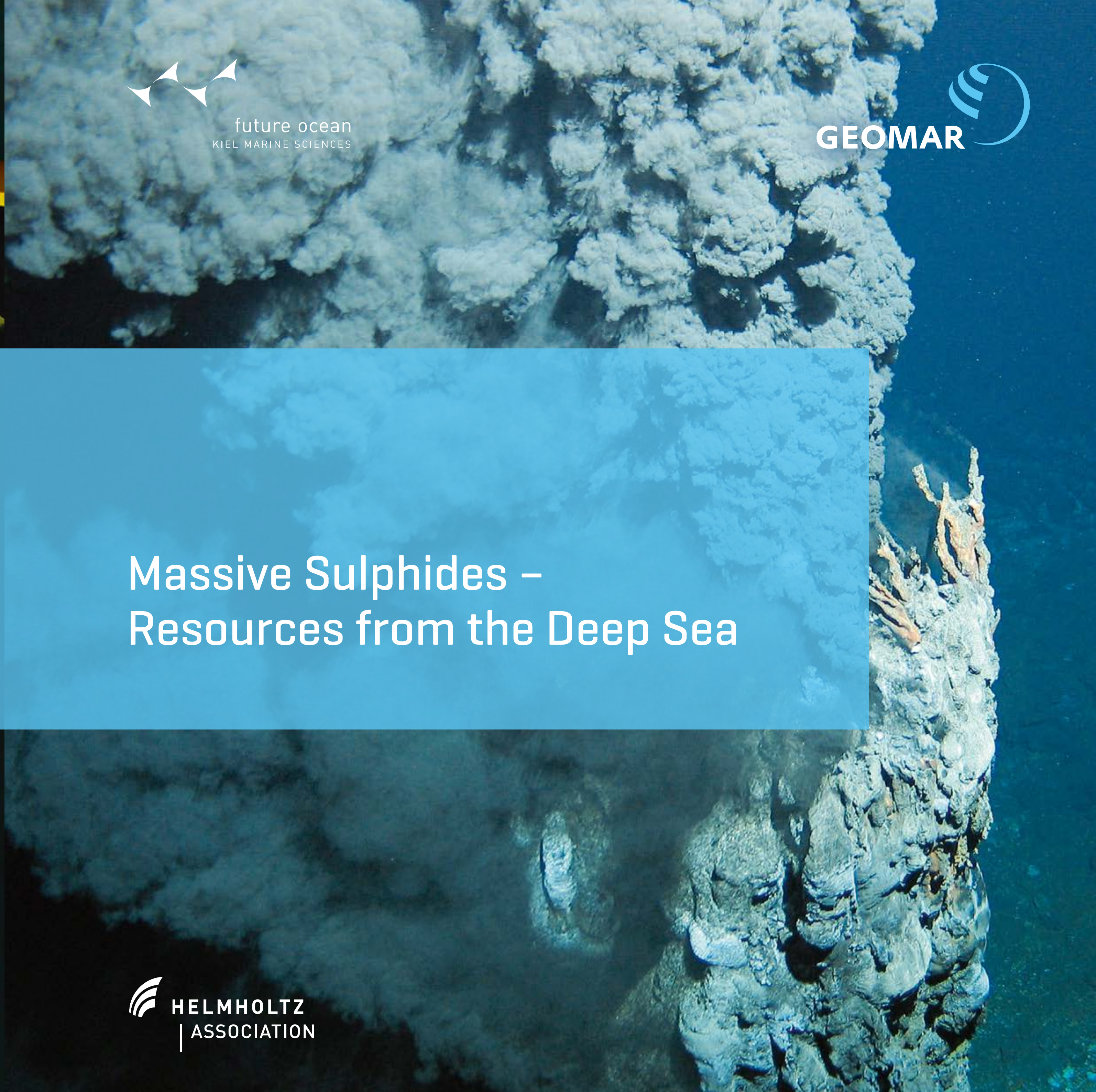

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Massive Sulphides – Resources from the Deep Sea

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Helmholtz Centre for Ocean Research Kiel

Prof. Dr. Peter M. Herzig
Director

Ladies and gentlemen,

Whether copper, zinc, gold or the now often mentioned rare earths — the demand for metal and mineral resources continues. Tapping new deposits is becoming increasingly difficult which, in combination with a high demand, is causing prices to rise. Currently, these resources are obtained from mineral deposits on land. Attention is now increasingly turning to submarine deposits. In the last decade, discoveries through marine research have paved the way for future use of these deposits. In 1979, when the first deep sea vents called black smokers were discovered, no one thought of these as future resources. Only when it was revealed that some of the sulphide deposits contained very high concentrations of metals did they become of interest. Now, the first concrete plans for the exploitation of these deposits in the sea have been developed. While economic aspects are a major driver, environmental protection is also a major consideration. The GEOMAR Helmholtz Centre for Ocean Research in Kiel has been conducting research on both living and non-living marine resources for many years. With an interdisciplinary research approach and in close cooperation with scientists from around the world, the many different issues related to the sustainable use of marine mineral resources are being carefully examined. Here, we summarize the current state of knowledge on this topic for the scientist and non-scientist alike.

I wish you an enjoyable and
hopefully informative read

Peter Herzig

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4 **ALL METALLIC RAW MATERIALS** that humans need at the moment are obtained on land; hence from only a third of the planet's surface. The oceans cover approx. 71% of the earth's surface, yet they are hardly being used. Even though minerals such as sand and heavy minerals, including diamonds, have been extracted from the shallow water regions of the oceans for centuries, the metal deposits in the deep sea have always been considered largely "out of reach". However, the continuing high demand and thus increasing prices for raw materials are focusing economic attention on deep sea mining.

Mussel field in the South Atlantic

Title: Black Smoker in the Atlantic

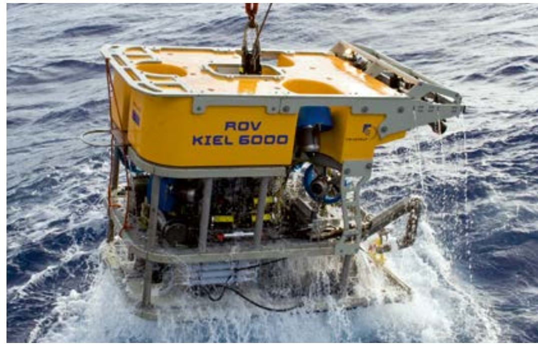
BLACK SMOKERS are outlet sites for hot fluids (over 400 °C) which contain various dissolved metals. In the example on the right, the vent of a black smoker is easily recognisable. The yellow fringe is made up of gold filled copper sulphides, the edge of zinc sulphides and other minerals.

The Sea Bed – A Source of Raw Materials for Humankind? 5

The sea bed is already an important source of resources for humankind. Sand and gravel as well as oil and gas have been mined from the sea for many years. Heavy minerals, such as diamonds, have been exploited off the coast of South Africa and Namibia for many years; titanium and gold have been mined along the coasts of Africa, Asia, Australia and North America. Obtaining raw materials from the sea is not a new practice. In future many other minerals will be added to this list. Recently, efforts to extend marine mining to the deep sea also have been advanced. Plans are already in place to exploit certain raw materials from the deep sea, including manganese nodules (found at depths of approximately 5,000 metres), cobalt crusts along submarine mountain ranges (generally between 1,000 and 2,500 meters), as well as massive sulphides and sulphide muds in areas of volcanic activity (from 500 to 5,000 metres water depth). Although these deposits are actively forming on the seafloor today, they are not renewable except at geological time scales. The metals in manganese nodules and cobalt crusts take millions of years to accumulate; large polymetallic sulphide deposits at black smoker vents take thousands of years to grow into economically interesting concentrations.

Left: The autonomous underwater vehicle AUV ABYSS carries out bathymetric mapping of large areas of the sea bed in the highest resolution (decimetre scale). The AUV is also equipped with chemical and physical sensors that can take measurements in the water column at 6000 metres depth.

Right: The remote controlled deep sea robot ROV KIEL 6000 can gather precise samples as well as deploy and recover scientific experiments on the sea bed. Like the AUV, the ROV can also reach a depth of 6000 metres.



Development of various metal prices between 2006 and 2015. Source: InfoMine.com

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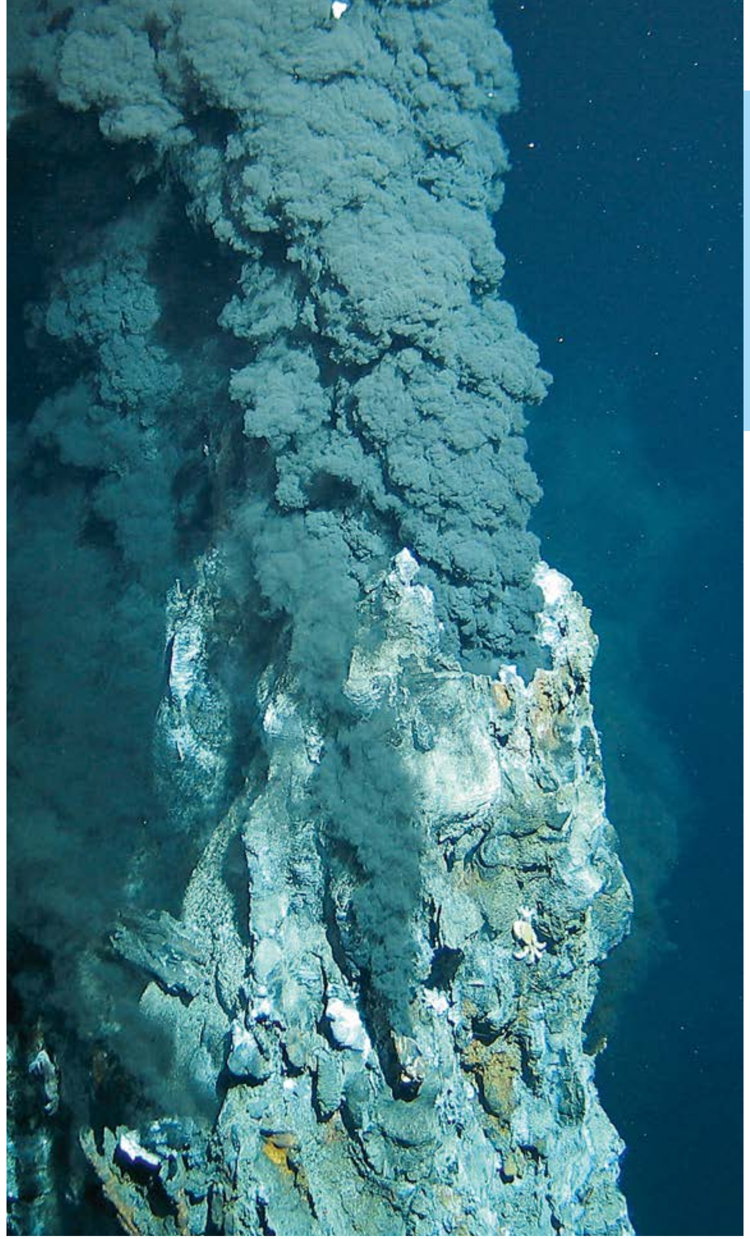
In the 1980s, partly influenced by predictions for raw material shortages by a group of economists known as the “Club of Rome”, interest in the raw materials of the deep sea reached a peak. Entire fleets of research vessels scoured the Pacific Ocean floor for manganese nodules containing recoverable concentrations of nickel, copper and cobalt. When the predictions of major shortages did not materialize, the interest of the industrialized countries dwindled. New deposits were found on land, and the prices of the metals decreased. However, this first marine mining “boom” and the sudden realization of the possible consequences of industrial exploitation of the sea led to the founding of the International Seabed Authority of the United Nations in Jamaica (ISA) as well as the signing of the “Constitution of the Seas” UNCLOS (United Nations Convention on the Law of the Sea) in 1982. Since it went into effect in 1994, this treaty has formed the basis for the use of resources from the sea bed outside of national jurisdiction. Renewed interest in marine resources in the last decade has been driven by sharply rising raw material prices and especially the strong economic growth of countries such as China and India. Short-term economic crises are unlikely to dampen this long-term trend or the growing demand for resources from the sea.



Black Smokers in the Atlantic.

THE BLACK SMOKER ACQUIRED ITS NAME due to the similarity to an industrial chimney. During the ascent through the sea bed, the metals are dissolved in the hot colourless fluid. When the hot fluid meets the cold, oxygen-rich sea water, the metals precipitate and turn the escaping solution black.

Massive Sulphides

Seafloor massive sulphide deposits are deposits of metals and sulphur that are formed by high-temperature hydrothermal vents (“black smokers”) at submarine volcanoes. Black smoker vents are common at submarine plate boundaries where volcanic activity meets sea water and there is an exchange of heat and mass between the hot volcanic rocks and the cold ocean water. At these locations, cold sea water sinks to depths of several kilometres into the sea bed along cracks and fissures. The sea water is heated to temperatures over 400 degrees Celsius close to the source of the molten lava and dissolves metals and sulphur from the rock that it flows through. At 400 degrees Celsius, the density of the heated sea water decreases sharply, and it rises very quickly to the sea bed where it is discharged at high pressure out of chimney like vents When the hot, metal and sulphur enriched solution meets the cold sea

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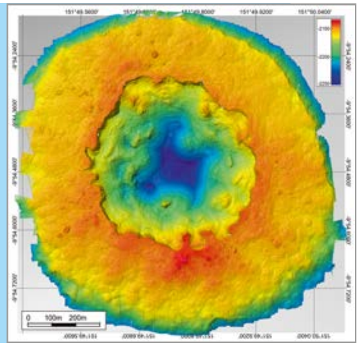
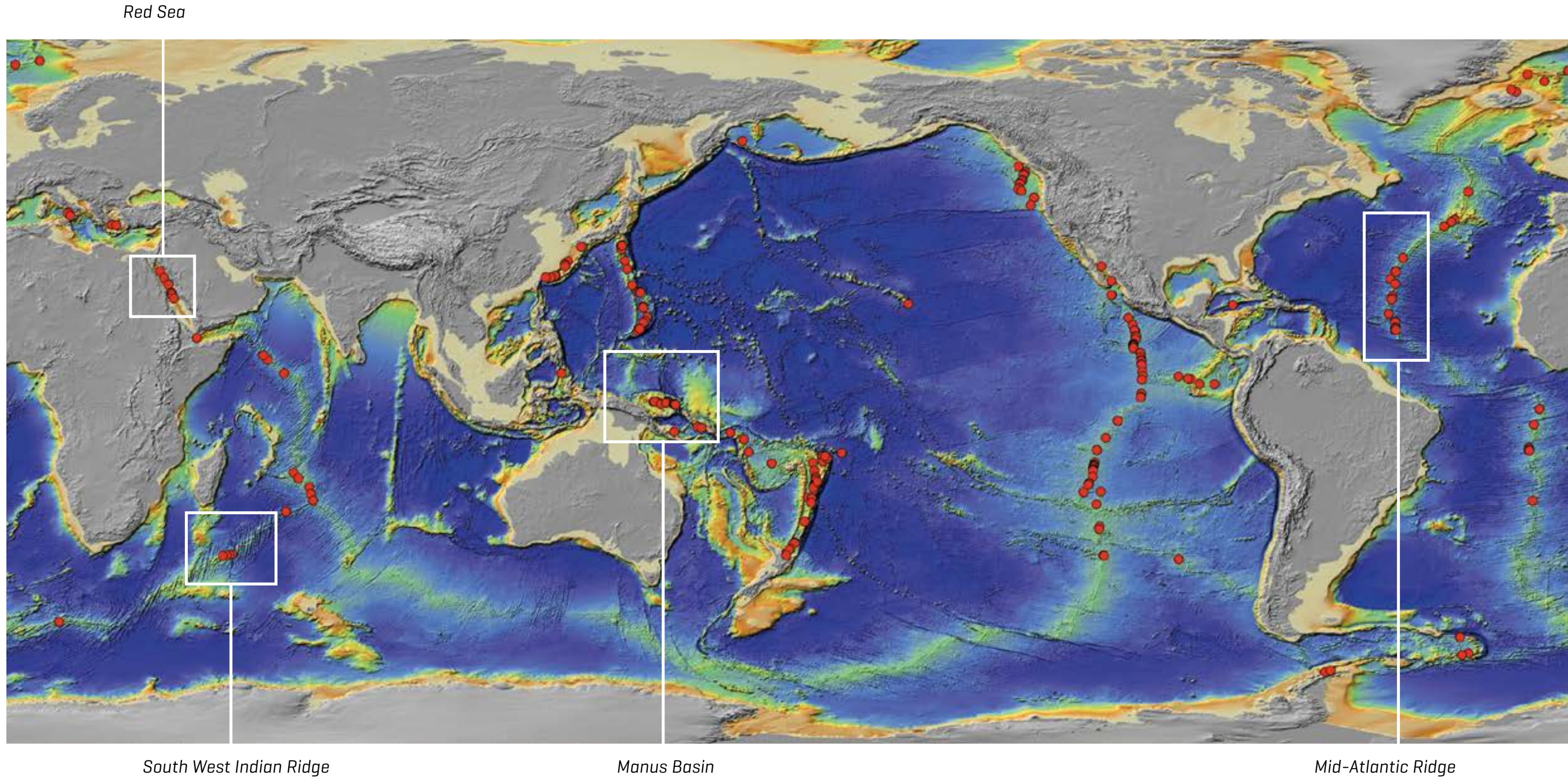
BLACK SMOKERS DEVELOP IN AREAS WITH high volcanic activity. However, the structures from which the hot fluid rises cannot be detected by ship based echo-sounders which are generally used for mapping the world's oceans. The ship based bathymetric mapping of a volcano in the Woodlark Basin, in which ores are suspected (left), is vague. Only high resolution mapping with deep diving, autonomous underwater vehicles such as the AUV ABYSS, allow a better understanding of the conditions in which these hydrothermal systems develop (right).



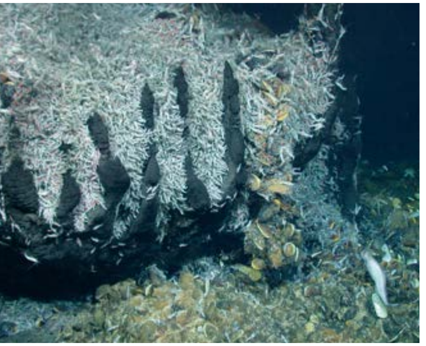
water, the dissolved metals precipitate as metal sulphide compounds and deposit on and under the sea bed as massive sulphide. These high-temperature vents are inhabited by micro-organisms that, without light, can obtain their energy through the oxidation of hydrogen sulphide. From a food chain based on this chemosynthesis, uniquely adapted biological communities with many endemic species have developed.

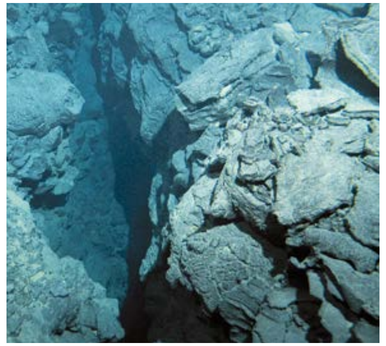
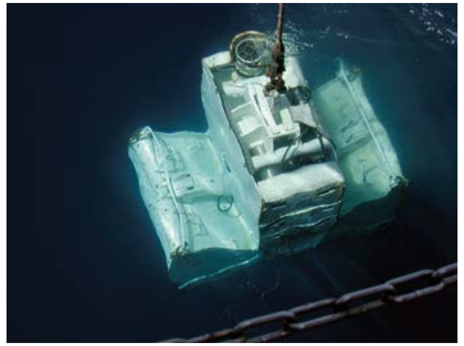
Frequency and Metal Content

Black Smokers were discovered in 1979 at the East Pacific Rise, where the oceanic plates are spreading apart at a rate of > 10 cm/year. For a long time it was assumed that the massive sulphides only developed at such fast-spreading mid-ocean ridges, as volcanic activity and heat production are very high there. Since 1979, more than 300 sites of high-temperature hydrothermal activity and sulphide deposition have been found, including on mid-ocean ridges that are spreading very slowly, such as the Mid-Atlantic Ridge. Large deposits or clusters of vents are found, on average, about



The distribution of black smokers and massive sulphide deposits in the world's oceans. Large areas, especially those in the southern oceans, have not been investigated yet and for this reason do not exhibit any deposits (Status 2015). Areas of special economic interest are highlighted.




From left to right:

A large number of shrimp graze at a sulphide structure in the Atlantic.

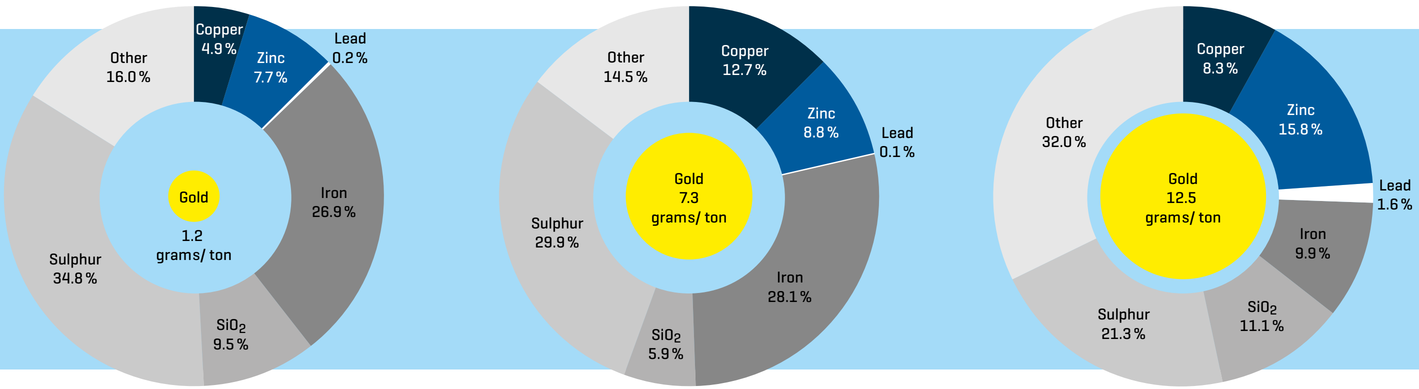
After successful sampling, the rocks are classified and described based on geological features.

The extraction of drilling cores such as this one from the Tyrrhenian Sea is indispensible when determining the tonnage and metal concentration within the massive sulphides.

A crevice in the sea bed where hot fluid can rise.

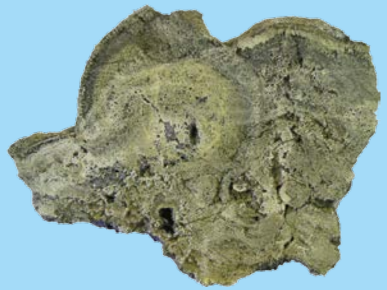
A remotely controlled gripper is used to take large samples of up to approx. 0,6 m^3.

A new smoker is beginning to grow on the sulphide crust.

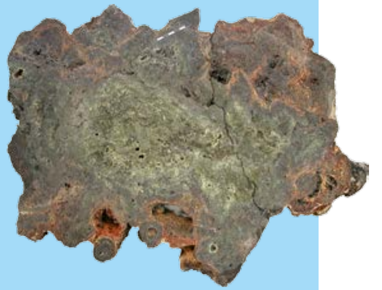


Metal content (% by weight) as well as gold content in massive sulphides from selected geological areas.

100 km apart along the mid-ocean ridges (closer together on fast-spreading ridges; farther apart on slow-spreading ridges). Although only a fraction of the ridges have been explored, the spacing of the known deposits suggest that there may be as many as 500 to 1,000 additional sites still to be discovered on the ridges. In the western part of the Pacific Ocean, another type of volcanic activity occurs where oceanic crust of the Pacific plate is subducted into the Earth's mantle, producing arc-like chains of submarine volcanoes and volcanic islands such as the Tonga-Kermadec arc. Even more black smoker deposits occur on these submarine volcanoes. Many of these deposits are located at a relatively shallow water depth (less than 2,000 metres) and lie in the exclusive economic zones of the neighbouring countries, making them attractive sites for future exploitation, both logistically and in terms of the technical challenges.
The concentrations of non-ferrous and precious metals in the deposits vary widely from region to region. The black smokers along the mid ocean ridges are mostly made of iron sulphides which are of little economic interest. Copper and zinc together generally make up less than 10 % of the deposit by mass. Gold concentrations are typically less than one gram per ton. A special type of deposit has developed on slow-separating ridges in the Atlantic and the Indian Ocean where large faults have exposed the Earth's upper mantle. Massive sulphides at these locations commonly have higher concentrations of copper and gold. Deposits that have been found in the Southwest Pacific, such as those in the Manus Basin of Papua New Guinea, have the highest copper and gold concentrations; making these deposits even more attractive targets for possible mining. A number of other economically important metals occur in trace but potentially recoverable concentrations (grams per ton). These are, amongst others, antimony, germanium, indium, tellurium and bismuth. The concentrations, however, vary greatly and research on their distribution is incomplete.



MASSIVE SULPHIDES are not always characterised by a high metal content. Many deposits, especially those along the Eastern Pacific ridge and around the Mid-Atlantic ridge are made up of iron and sulphur compounds (left). These are not as interesting economically as deposits on land since considerably richer deposits can be mined in open pits. Only deposits with accumulated metals such as copper, zinc and a series of trace metals are being sought after at present. The sample on the right shows the cross section of a black smoker from the eastern Manus basin off Papua New Guinea. The difference between the copper enriched core and the brown zinc enriched outer section is clearly visible. The average gold content for this sample is 15 grams per ton of ore.



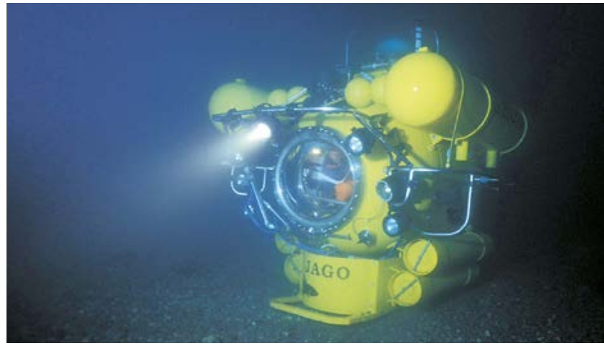
Size of Deposits and Commercial Interest

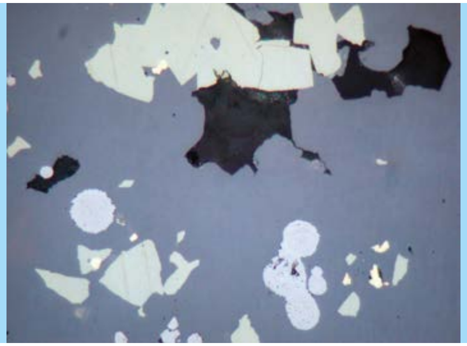
There are also enormous differences in the sizes (tonnage) of the deposits. Most have a diameter of less than a few 10s of metres and contain only little material (a few 1,000 tons to 10,000 tons). A number of the known deposits on the mid-ocean ridges are estimated to contain between 100,000 tons and 1 million tons of massive sulphide, and a few may be as large as 10 million tons. Up until now only a small number of massive sulphide deposits are known that are large enough to be of economic interest.

The largest known sulphide deposit (Atlantis II Deep) is located at a depth of 2,000 metres in the Red Sea where tectonic forces are causing Africa and the Saudi-Arabian peninsula to drift apart. Here, the metals are deposited from large pools of dense brine, rather than from black smokers, forming thick deposits of metalliferous mud (90 million tons) containing copper (0.5%), zinc (2 %), silver (39 grams per ton) and gold (0.5 grams per ton). This deposit was discovered in the 1960s and recovery of the mud from the seafloor was tested successfully in the early 1980s. The value of the deposit was estimated at the time to be approximately US $ 13 billion.

Bottom left: Releasing the ROV KIEL 6000 (Photograph: B. Grundmann).

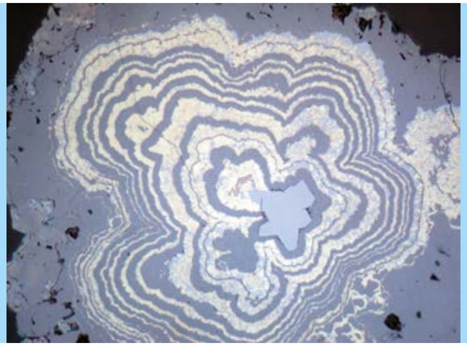
Bottom right: Exploring the sea bed with the manned submersible JAGO.





Ore microscopy plays an important role in the analysis of massive sulphides. The samples are polished and examined in the reflected-light microscope for mineral components. This is the only way to find out how gold, for example, turns up in the sample. On the left, little, light yellow gold traces are bound in different sulphides. The size of the grains of gold is between 2 and 10 micrometres.

A chat of pyrite (FeS_2, creamy white) with haematite (Fe_2O_3, light grey) and magnetite (Fe_3O_4, medium grey). The darker shades are voids and portray the high porosity of the sea bed ores. Width of picture: approx. 0.1 mm.



Many massive sulphides show signs of zonal structures in microscopic images which resemble the annual growth rings in trees. In the left example the physicochemical characteristics of the hot fluid change very quickly and form alternating sequences of zinc sulphides (ZnS, medium grey) and copper sulphides ($CuFeS_2$, yellow, light grey, brown). Width of picture: 0.03 mm.

In 2010 a 30-year mining licence for this deposit was granted; however it is not known when the mining will begin. Interest in seafloor massive sulphides in international waters has also increased dramatically in the last few years. Since 2011, 6 countries have applied for exploration contracts for massive sulphides in the Indian Ocean and the Atlantic. This includes Germany, China, Russia, France, South Korea, and India. Since May 2015 the German Geological Survey (Bundesanstalt für Geowissenschaften und Rohstoffe, BGR) in Hannover holds a contract area of 10.000 km^2 in the central Indian Ocean that will be investigated for its resource potential for the next 15 years, the runtime of the contract. Several commercial companies are also interested in mining these ores, for example in the territorial waters of Papua New Guinea and New Zealand. One company received the first mining licence for a 2-million ton seafloor massive sulphide deposit in Papua New Guinea in January 2011 and the mining is expected to begin in early 2018. The current in situ value of the metal contained in this deposit is around US$ 1 billion.

Presently the mining of massive sulphides in the territorial waters of countries in the West Pacific (e.g., Papua New Guinea) seem the most probable, as the relatively high concentrations of precious metals here would generate more value for the individual companies. However, because of the sizes of many of the deposits, which are generally smaller than those of comparable deposits being mined on land, it can not be assumed that marine mining of massive sulphides will compete in the short term with metal mining on land. More likely, it will be one of a number of different sources from which metallic mineral resources are extracted in the future.

Left: The research vessel METEOR has been used mostly for work in the Atlantic since 1986.

Centre: The new research vessel SONNE has been employed for work in the Pacific and Indian Oceans since 2015. Photo: T. Badewien, ICBM

Right: The research vessel MARIA S. MERIAN works mainly in the Atlantic and adjacent seas.

Effects of Marine Mining

The environmental effects of massive sulphide mines on the sea bed are unknown. Although the deposits have a relatively small "footprint" on the seafloor, the biological communities at active black smokers would be at risk. Some argue that the endemic fauna are well adapted to major disruptions, such as volcanic eruptions. The mining of ores from active black smoker deposits would not cut off the supply of hot solutions from the subsurface, thus the recolonisation of surrounding hot vents after the mining has ceased is likely. In Papua New Guinea, areas of active hydrothermal venting have been set aside that would enable recolonisation or resettlement. But, the exact process of recolonization is not yet clear. For this reason, future mining is planned only in areas where hydrothermal activity has ceased and where vent fauna have abandoned the site. A considerable amount of research is needed before the protection of the seabed from the effects of mining can be assured, and this research is ongoing.

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GEOMAR investigates the ocean from the sea bed to the atmosphere. Emphasis is laid on the role of the ocean in climate change, human affects on marine ecosystems, marine resources and marine natural hazards. The research foci are integrated in four central areas: ocean circulation and climate dynamics, marine biogeochemistry, marine ecology and dynamics of the ocean floor.

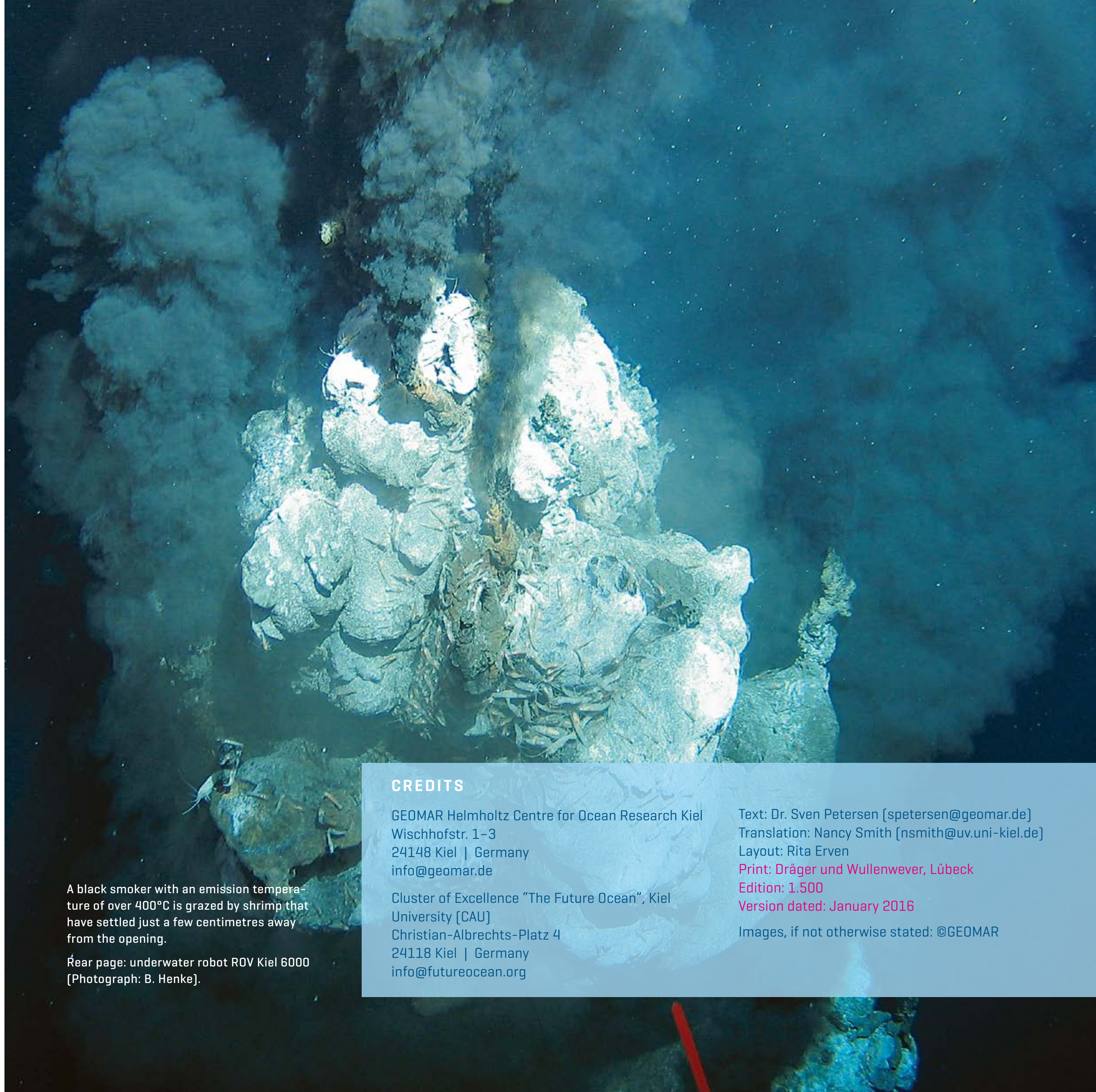
Several long term research projects are carried out in close cooperation with Kiel University, the Cluster of Excellence "The Future Ocean" and the collaborative research centres of the German Research Foundation. The approx. 950 staff members use the newest methods in their research and communicate their research results to students and young researchers. GEOMAR operates four research vessels, the manned submersible JAGO, four deep sea robots, complex monitoring devices, various specialised laboratories as well as high resolution climate and ocean models.

The Future Ocean – Kiel Marine Sciences

The ocean, through its dominating influence on global climate and its growing role as a source of natural resources but also of devasting hazards, plays a key role in the lives of all human beings. The Cluster of Excellence "The Future Ocean" pursues a research approach that is unique in Germany: marine researchers, geologists and economists join forces with mathematicians, computing, medical, legal, and social scientists to investigate ocean and climate change from a multidisciplinary perspective. A total of over 200 scientists from Kiel University (CAU), the GEOMAR Helmholtz Centre for Ocean Research Kiel, the Institute for the World Economy (IfW) and the Muthesius Academy of Fine Arts are using innovative means to share their findings with the international scientific community, stakeholders, decision makers, civil society and the public at large because they believe that by understanding the ocean we can sustain our future.

Left: The AUV ABYSS moves towards the research vessel Meteor after an operation.

Right: Mobile drilling equipment, for example from the British Geological Survey, is used to explore the sub surface.



A black smoker with an emission temperature of over 400°C is grazed by shrimp that have settled just a few centimetres away from the opening.

Rear page: underwater robot ROV Kiel 6000 (Photograph: B. Henke).

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